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Nicholas J. Turro				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)				
Columbia University New York, NY 10027				
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Supramolecular photochemistry provides experimental tools and mechanistic concepts pertinent to the examination of the fate of Air Force chemicals and how they may be photochemically transformed into environmentally benign substances. This beneficiation process of converting AF chemicals to environmentally benign materials is termed mineralization. A "biomimetic" strategy is adopted for which the laboratory model of beneficiation is based on processes occurring in nature. This biomimetic model provided us with the strategy of employing supramolecular photochemical systems to achieve the mineralization of AF chemicals via photosensitized degradation.				
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**A SUPRAMOLECULAR APPROACH TO THE MECHANISMS
OF PHOTOMINERALIZATION OF HAZARDOUS
MATERIALS**

**Nicholas J. Turro
Department of Chemistry
Columbia University
New York, NY 10027**

November 4, 1996

**Final Technical Report for the period
1 February 1995 through 31 July 1996**

Prepared for

**Air Force Office of Scientific Research
Building 410
Bolling Air Force Base, DC 29332**

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Final Technical Report

I. Abstract of Technical Progress Two approaches were utilized in the discovery and invention of Air Force materials converting potential environmental hazards into environmentally benign materials. The first feature involved the excitation with light of model hazardous materials and the initiation of chemical steps which either cascade to cause degradation or produce materials that are readily degraded into environmentally benign substances. The second feature involved a multidisciplinary attack on the investigation of the degradation mechanism through the use of a range of state of the art spectroscopic techniques to characterize the structure and dynamics of reactive intermediates generated by photochemical excitation. The specific systems investigated have employed time resolved electron spin resonance and time resolved optical absorption and emission to characterize reactive intermediates. Photoinduced electron transfer has been shown to possess excellent potential to serve as a general method in initiating the photodegradation of a range of hazardous materials such as high energy fuels and fluorinated hydrocarbons.

II. Accomplishments/New Findings During the first year of the project progress was made in two areas: (1) the mechanism of photodegradation of quadricyclane, and (2) the mechanism of photodegradation of high performance fluorocarbon polymers. In area (1) we studied the ESR of photosensitizers capable of reducing and oxidizing quadricyclane as a key first step in its degradation. The mechanistic concepts which drove these studies are that initial acceptance of an electron by quadricyclane or removal of an electron from quadricyclane initiates degradation. We were successful in detecting the ESR signal of the hydrated electron (e_{aq}^-), a powerful reducing agent. A paper was published in the *Journal of the American Chemical Society*.

Additionally, we have produced the radical cation of quadricyclane by alternate synthesis through the photosensitized loss of nitrogen from cyclic azoalkane derivatives. Through the use of chemically induced dynamic nuclear polarization (CIDNP) we have detected the radical cation of quadricyclane and its conversion to norbornadiene radical cation. A paper on the initial phases of this project has been published in the *Journal of the American Chemical Society*.

In area (2) we have demonstrated that the photosensitized decomposition of fluorocarbons can be readily achieved. As a model substrate, perfluorodecalin was investigated and found to be readily converted to 9,10-unsaturated olefin and the photosensitizer employed. In this project we attempted to convert the olefin to the completely

defluorinated aromatic compound.. From this model system, we investigated the photosensitized decomposition of samples of perfluoropolyalkylether sent to us by Dr. L. Gschwender from Wright Laboratory at Wright-Patterson Air Force Base, Ohio. These perfluoropoly-alkylethers are representative of spilled materials studies used in gas turbine engine oils. This work has been published in *Tetrahedron Letters*.

III. Cumulative List of Publications:

1. N.J. Turro, I.V. Khudyakov, and H. van Willigen, "Photoionization of Phenothiazine: ESR Detection of Reactions of the Polarized Solvated Electron, *J. Am. Chem. Soc.*, **117**, 12273 (1995).
2. G.W. Sluggett, N.J. Turro, and H.D. Roth, "Electron Transfer Induced Deazatization of Cyclic Azo Derivatives of Quadricyclane and Norbornadiene," *J. Am. Chem. Soc.*, **117**, 9982 (1995).
3. N.A. Kaprinidis and N.J. Turro, "Photosensitized Defluorination of Saturated Perfluorocarbons," *Tetrahedron Letters*, **37**, 2373 (1996).
4. M.F. Ottaviani, N.J. Turro, S. Jockusch, and D.A. Tomalia, "Aggregational Process of the Positively Charged Surfactants CTAC and CAT16 in the Presence of Starburst Dendrimers: An Electron Paramagnetic Resonance Spectroscopic Study," *Colloids and Surfaces*, **115**, 9 (1996).
5. M.F. Ottaviani, C. Turro, N.J. Turro, S.H. Bossmann, and D.A. Tomalia, "Nitroxide-Labeled Ru(II) Polypyridyl Complexes as EPR Probes of Organized Systems. 3. Characterization of Starburst Dendrimers and Comparison to Photophysical Measurements," *J. Phys. Chem.*, **100**, 13667 (1996).
6. M.F. Ottaviani, N.J. Turro, S. Jockusch, and D.A. Tomalia, "Characterization of Starburst Dendrimers by EPR. 3. Aggregational Processes of a Positively Charged Nitroxide Surfactant," *J. Phys. Chem.*, **100**, 13675 (1996).

IV. Personnel Supported

Dr. Igor Khudyakov
Dr. Nikolaos Kaprinidis

V. Coupling Activities

Dr. Susan E. Burns, a postdoc of Prof. John Hassett of SUNY, Syracuse visited the PI's Laboratories on 4/29/95 to discuss the AFOSR project.

Lois Gschwender from Wright-Patterson AFB, OH sent us two samples of perfluoropolyalkylethèr for chemical/biochemical fate of spilled material studies used in gas turbine engine oils. The photosensitized decomposition of these materials was investigated.

Dr. Nikolaos Kaprinidis (post-doc in the PIs Laboratories) attended a Joint USAF/Army Contractor/Grantee Meeting on 6/8 and 6/9 1995 in Boulder, CO and presented a paper on "Photochemical Effects on Fate and Transport of Hazardous Aerospace Materials".

New Discoveries, Inventions, or Patent Disclosures: None

Honors/Awards: Distinguished Alumnus Award, California Institute of Technology, May 1996.